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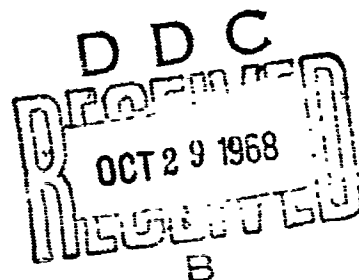
THE RAMAN SPECTRUM OF CRYSTALLINE LITHIUM NITRATE

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R. E. Miller, R. R. Getty, K. L. Treuil, and G. E. Leroi

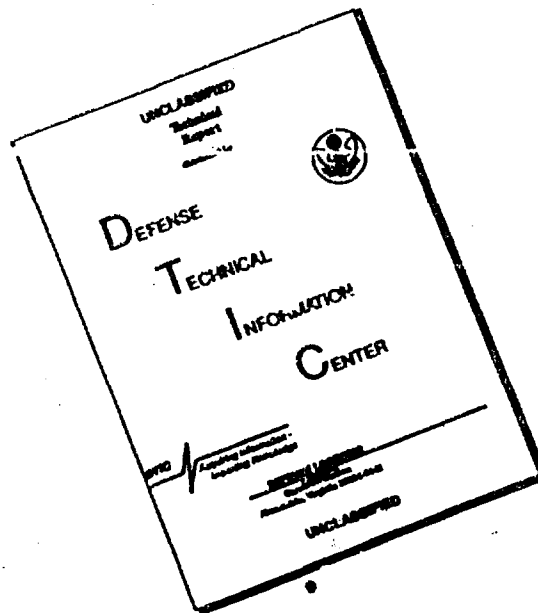(Submitted for publication in the Journal of Chemical Physics)

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THE RAMAN SPECTRUM OF CRYSTALLINE LITHIUM NITRATE

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ABSTRACT

Polarized Raman spectra of an anhydrous single crystal of $LiNO_3$ have been obtained under optimum experimental conditions. The internal vibrations of the nitrate ion are observed as follows: $\nu_4(E_g) = 735._4$, $\nu_1(A_{1g}) = 1071._0$ and $\nu_3(E_g) = 1384._6$ cm^{-1}; these frequencies are essentially independent of the cation in the host lattice. The two Raman-active (E_g) lattice modes have been located and assigned to primarily translational ($124._4$ cm^{-1}) and librational ($237._2$ cm^{-1}) motions. No indication of coupling between these vibrations is observed. The frequencies of the external vibrations relative to those of $NaNO_3$ demonstrate that they are dependent on the volume of the crystalline unit cell. Except for small intensity contributions in some orientations which are probably due to depolarization effects in the birefringent crystal, the polarizability activities of both the internal and external modes follow the expected symmetry selection rules.

INTRODUCTION

Raman scattering has been observed from $LiNO_3$ in the solid,[1] melt,[2] and solution,[3] and the results discussed by several authors.[1-5] However, there have been no reported attempts to conduct a polarization study of an anhydrous single crystal, or to locate the Raman-active external lattice frequencies of the solid. Lithium nitrate crystallizes in the calcite structure (D_{3d}^6 space group) with the nitrate ions occupying D_3 sites and the lithium ions S_6 sites.[6] Thus five Raman-active fundamental vibrations are expected.[7] Three are attributable to internal vibrations of the nitrate ion: $v_1(A_{1g})$, $v_3(E_g)$, and $v_4(E_g)$; the previous results for these vibrations in the various phases of $LiNO_3$ have been summarized by Bues.[2] The remaining Raman fundamentals are E_g external (lattice) oscillations. The normal modes of the lattice vibrations were depicted in our previous work on $NaNO_3$;[8] for convenience they are reproduced in Fig. 1. Although one of the vibrations is translational in character and the other librational, since they have the same symmetry mixing is allowed. It would be interesting to know whether the nature of the cation affects the degree of mixing, which was found to be undetectable for sodium nitrate.[8]

The Raman frequencies for NO_3^- internal modes in the solid, melt, and solution for a series of alkali nitrates have been compared by Bues,[2] who interpreted the small shifts in the symmetric stretching frequency v_1 (less than 4%) according to a "free volume" model. Even smaller frequency differences were noted for v_3 and v_4, and it was argued that these motions should be less sensitive to the packing of the environment. However, it was also shown that the internal frequencies in $LiNO_3$ are quite dependent on the amount of water present and the physical state of the sample.[2,3] If the solid samples used in

the early studies were not of the highest quality, for example because of the extremely hygroscopic nature of lithium nitrate, incorrect frequencies would have been observed for the crystal. This would significantly affect the hypothesis formulated to explain the small frequency shifts in the NO_3^- vibrations with change in cation.

Anomalous polarization intensity ratios for the Raman bands of crystals with the calcite structure have been generally observed, and interpreted for $CaCO_3$[9] and $NaNO_3$[8] as being primarily due to depolarization of the incident and/or scattered light in the optically anisotropic crystals. Since the ratio of the molecular refractivity, a measure of birefrigence, is almost the same for sodium and lithium nitrates,[10] a careful polarization study of crystalline $LiNO_3$ should provide a test for this explanation.

Finally, in an interpretation of the infrared combination spectra of calcite and the alkali nitrates, Schroeder, Weir, and Lippincott[11] suggested that a torsional lattice vibration about the optic axis should exist with a fundamental frequency of 20-30 cm^{-1}. Although such a vibration should be Raman-inactive by symmetry, it was reported in early studies of calcite;[12,13] it was not observed in later investigations of $NaNO_3$[8] and $CaCO_3$.[9] Since measurements in the low frequency region were difficult due to scattered light and grating ghosts, it seemed worthwhile to confirm the absence of the torsional motion in the case of $LiNO_3$.

In order to determine the external lattice vibration frequencies of $LiNO_3$ and to unambiguously establish the internal nitrate ion frequencies, as well as to study the effect of the alkali cation on these vibrations, the Raman spectrum of a large, anhydrous single crystal of lithium nitrate has been obtained. Using modern Raman instrumentation a complete polarization study has been made, and the available spectra region extended to within 10/cm^{-1} of the exciting radiation.

EXPERIMENTAL

The crystal used in this investigation was obtained from the Harshaw Chemical Company. Unfortunately, unlike $NaNO_3$, a clear, homogeneous single crystal of $LiNO_3$ can be grown only with some difficulty, and cannot be controllably cleaved. The sample received in our laboratory was a cube approximately 5mm on a side, polished to size from a larger ingot. The faces were mutually perpendicular within $1°$, and the z-axis (optic axis) was normal to one of them. In order to facilitate orientation, the crystal was mounted in a W and W eucentric goniometer which had been placed in a small Plexiglass drybox. This ensured that the sample remained anhydrous; at no time was the crystal exposed to the room atmosphere.

The oriented single crystal was first irradiated using a Spectra-Physics Model 125 He-Ne laser emitting about 70 mW at 6328Å. The $90°$ scattered light was collected by appropriate optics, dispersed by a Spex Model 1400 double monochromator, and detected using a thermo-electrically cooled ITT FW-130 photomultiplier (S-20 response). The photomultiplier output signal was amplified with a Victoreen VTE-1 micro-microammeter, and displayed on a Moseley 7100B strip chart recorder.[14] The laser power was adequate to discern the general features and intensity patterns of the Raman spectrum. More detailed studies of each band were made using a Spectra-Physics Model 140 argon ion laser emitting about 600 mW at 4880Å and 700 mW at 5145Å as the excitation source.

In general, the spectra were obtained with the incident beam focused within the sample using a solid angle of less than $2°$, and with the scattered light gathered using f/2 optics. Depending on the band being studied and the polarization conditions, spectral slit widths in the range 0.2 - 2 cm^{-1} were

employed. The accuracy of the reported frequencies is within 0.5 cm^{-1}. All measurements were made at room temperature.

RESULTS AND DISCUSSION

As indicated in the third column of Table I, for a rhombohedral crystal with D_{3d} symmetry only four of the polarizability tensor derivatives are unique. According to the group theoretical analysis α_{xx} and α_{yy} are always related due to symmetry, as are α_{xz} and α_{yz}. Representative Raman spectra of crystalline $LiNO_3$ in the xx-, zz-, xy-, and xz-orientations are shown in Fig. 2. The polarization is specified by the commonly accepted notation[15] of the type x(yz)y, where the initial and final letters denote the direction of the incoming and observed light in the crystal coordinate system, and the letters in parenthesis indicate the polarization axes of the incident and scattered radiation. Thus in this example a measure of the α_{yz}-component of the polarizability tensor derivative would be obtained.

The observed frequencies, assignments, and relative intensities as a function of polarization are summarized in Table I. Theoretical considerations of the relative intensities have been developed by Bhagavantum[16] and Saksena.[17] Like the other crystals in its class, lithium nitrate is highly birefringent, and therefore anomalous depolarization effects, such as the presence of a given vibration in a polarized spectrum where it is theoretically forbidden, are to be expected. Fig. 2 shows that such small residual intensity is sometimes observed. This subject has been considered in the discussions of the Raman spectra of calcite[9] and sodium nitrate.[8] Furthermore, in the course of checking the polarized spectra using alternate incident and scattered light axes, it was

observed that the relative intensities of the bands sometimes changed although the same tensor component was being observed. This effect is most striking for v_1 in the α_{xy} polarization, which is shown in Fig. 3. Again the optical inhomogeneity of the LiNO$_3$ can account for this observation, as discussed in detail for the case of calcite by Porto, et al [9]

A. Internal Modes

The symmetric stretching vibration (v_1) of the NO$_3^-$ ion in crystalline LiNO$_3$ is observed at 1071.$_0$ cm^{-1}. This frequency is close to that observed[8] for NaNO$_3$ ($v_1 = 1068$ cm^{-1}), but appreciably different from the value of 1086 cm^{-1} previously reported for solid LiNO$_3$,[1] which was used in the subsequent discussion of frequency trends among various alkali nitrates.[2-5] Detailed scans of the v_1 region in the yy-polarization using the approximately 0.7 watt of power available in each of the argon ion laser lines at 4880 Å and 5145 Å showed the presence of a sharp band at 1050 ± 1 cm^{-1} with an intensity about 1/200 of the strong peak at 1071 cm^{-1}. The relative intensity suggests that the weak band at 1050 cm^{-1} is due to the v_1 vibration of a nitrate ion containing one oxygen -18 atom.[18] Calculation of the isotopic frequency assuming a valence force field and a planar geometry for the XYZ$_2$ molecule[19] gives excellent agreement with the observed value, thus confirming this assignment.

The antisymmetric stretching vibration (v_3) is located at 1384.$_6$ cm^{-1}, a value slightly lower than the previously reported[1] frequency of 1391 cm^{-1}, but essentially identical to v_3 of the nitrate ion in NaNO$_3$, which is observed[8] at 1385 cm^{-1}. Careful examination of this spectral region using argon ion excitation revealed a weak band at 1354 cm^{-1}. Isotope shift calculations suggest the assignment of this band to v_3 of ^{15}NO$_3^-$ ions, present in 0.37% natural abundance.

The remaining internal fundamental, the in-plane bending motion, v_4 is observed at 735.$_4$ cm^{-1}. This frequency is slightly higher than that listed by Pues[1] (728 cm^{-1}), and also higher than the value observed[8] for $NaNO_3$ (724 cm^{-1}). The frequency shift of 1-1/2% in the vibration upon change in cation, although the largest for the internal modes, confirms that the bonding in the nitrate ion is essentially unaffected by the packing in the crystal. None of the fundamentals show frequency shifts of sufficiently significant magnitude to be correlated with the available "free volume" in the various respective crystal lattices.

The depolarization behavior exhibited by the internal vibrations, shown in Fig. 2, closely follows expectation. For the E_g modes, v_3 and v_4, the group theoretical selection rules predict that the allowed polarizability components are $\alpha_{xx} = -\alpha_{yy} = \alpha_{xy}$ and $\alpha_{xz} = \alpha_{yz}$. However, it is expected that the intensity in the xz- and yz-spectra will be relatively weak,[17] since in the limit of an isolated nitrate ion (D_{3h} symmetry) the out-of-plane polarizability derivative components approach zero during the in-plane vibrations. The absence of v_3 and v_4 in the x(zy)z-spectrum of Fig. 2 demonstrates that there is little interionic coupling in the $LiNO_3$ lattice. It is satisfying to note that the intensities of these bands in the yy- and xy-spectra are indeed quite similar.

For the A_{1g} symmetric stretching vibration, v_1, the only nonvanishing polarizability derivatives should be $\alpha_{xx} = \alpha_{yy}$ and α_{zz}. In addition, symmetry considerations suggest[17] that $\alpha_{yy}^2 > \alpha_{zz}^2$. The intensity ratio $(\alpha_{yy}^2/\alpha_{zz}^2)$ is approximately 10 for the 1071 cm^{-1} band of $LiNO_3$; the corresponding ratio is also 10 for $NaNO_3$,[8] and is about 5 for $CaCO_3$.[9]

The v_1 band also appears weakly in the x(yx)y-spectrum of Fig. 2,
and is barely discernible in the x(zy)z orientation; in both cases it should
be absent. Furthermore, as shown in Fig. 3, the relative intensity of the
1071 cm^{-1} band in the xy-polarization is much higher when the crystal is rotated
so that light either enters or is gathered along the crystallographic z-axis.
This striking orientation dependence is clearly due to the particular properties
of the $LiNO_3$ crystal, and not to an inherent breakdown of symmetry selection
rules. Indeed, such behavior is expected for highly birefringent crystals,
if either the incident or scattered light is convergent. This effect has been
discussed in detail by Porto, Giordmaine, and Damen,[9] and is also observed in
calcite[20] and sodium nitrate.[8] If the incident polarized light is not extremely
well collimated and colinear with the intended crystalline axis interference
between the ordinary and extraordinary components of other polarizations will
contribute to the scattering. For example, in our z(yx)y spectrum depolarized
z(xx)y light, where v_1 is strongly allowed, would also be detected. Similarly,
since the scattered radiation is collected over a finite solid angle, contributions
from unwanted polarizations will also be measured. Thus depolarized scattering
from x(yy)z will be contained in our x(yx)z-spectrum. The dependence of these
effects on solid angle has been discussed by Porto, et al;[9] depolarization is
important for divergence angles as small as 1°. In our experiments the half-
angle of the focused incident light was about 0.5°, whereas the scattered
radiation was collected over a cone with angle of approximately 16°. Thus the
anomalous α_{xy} - intensity for v_1 would be expected to be stronger in the x(yx)z-
spectrum than in z(yx)y; this is borne out in Fig. 3. These interference effects

are minimized in the x(yx)y geometry, since depolarization of the incident

or scattered light gives rise to zx- or yz-polarizations, where the A_{1g}

vibration is also forbidden. The weak appearance of ν_1 in the x(yx)y spectrum

must therefore be attributed to crystalline imperfections or misalignment of the

sample in the laser beam. Since the crystal orientation was adjusted to optimize

the intensity expectations, it is likely that the unavoidable, natural imperfec-

tions in the $LiNO_3$ sample are responsible for most of the slight residual intensity

The Raman spectra shown in Figs. 2 and 3 were obtained with the He-Ne

laser. The higher power Ar^+ laser was also used, and the spectra were again

of excellent quality. The higher scattering intensity permitted narrower slits

to be used, but no new fine structure was thus revealed. However, when slits

comparable to those in the He-Ne experiments were employed, giving scattering

due to the internal fundamentals far above the normal intensity scale, new, weak

spectral features were observed. In addition to the isotopic bands mentioned

above, several combination bands were observed. The peak located at 1675 ± 1 cm^{-1}

is assigned to $2\nu_2$; thus the out-of-plane NO_3^- bend, ν_2, which is infrared-active

only, should occur at about 840 cm^{-1}. Again, comparison to crystalline $NaNO_3$,

where $2\nu_2$ is observed[21] at 1677 cm^{-1}, confirms that the internal vibrations of

the nitrate ion are relatively insensitive to the change in cation. The bands

observed at 1460 ± 2, 2115 ± 3 and 2134 ± 2 cm^{-1} are assigned as $2\nu_4$, $\nu_3 + \nu_4$,

and $2\nu_1$, respectively. In each case the effects of anharmonicity are quite

small. Another very weak band is found at 2159 ± 3 cm^{-1}, which cannot be readily

assigned. It should be noted that even under the intense argon-ion excitation

no evidence of Raman scattering due to combinations between nitrate ion internal

modes and the external (lattice) vibrations could be observed.

B. Lattice Modes

The low frequency region of the Raman spectrum of crystalline $LiNO_3$ was investigated to within about 10 cm^{-1} of the exciting line. No evidence of the postulated low-frequency torsion around the optic axis was noted, even with the higher power exciting lines. Two lattice vibrations are observed (Figs. 2, 3) at $124._4$ cm^{-1} and $237._2$ cm^{-1}, and are attributed to the expected translational and librational normal modes, in analogy to sodium nitrate.[8] These assignments are supported by the depolarization ratios of the two bands, which are summarized in Table I. Both vibrations are of E_g symmetry, where the allowed polarizability components are $\alpha_{xx} = - \alpha_{yy} = \alpha_{xy}$ and $\alpha_{xz} = \alpha_{yz}$. However, as Saksena[17] has shown, the in-plane translation should have $\alpha_{xz} = \alpha_{yz} \approx 0$ and the out-of-plane libration should have $\alpha_{xx} = - \alpha_{yy} = \alpha_{xy} \approx 0$, if the coupling between the vibrations is small. This is precisely the behavior shown in Figure 2, where the 124 cm^{-1} band (translation) is absent in the x(zy)z-spectrum, and the intensity of the 237 cm^{-1} band (libration) is smallest in the x(yy)z-spectrum. The latter intensity is even slightly lower than in the x(zz)y-spectrum where E_g bands are not allowed by symmetry. The residual zz-scattering probably arises from the birefringence effects discussed above. In each polarization the $LiNO_3$ spectra are superior to those previously reported[8] for $NaNO_3$; since the crystals have similar birefringence, it is likely that crystal imperfections contribute most to the additional anomalous intensity in sodium nitrate. In neither crystal was evidence of mixing between the lattice modes apparent.

Unlike the internal fundamentals, the lattice frequencies are highly dependent upon the cation. The librational frequency is 1.9 times that of the translation in each case, but the $LiNO_3$ vibrations are a factor of 1.27 higher in frequency than the corresponding $NaNO_3$ bands. As Figure 1 shows, this cannot be attributed to the lighter mass of the lithium ion, since the cation is not involved in either Raman-active normal mode. However, it is quite reasonable that these relatively large-amplitude low-frequency nitrate ion vibrations will be dependent on the unit cell volume. Indeed, the volume of the $NaNO_3$ unit cell is approximately 30% larger than that of $LiNO_3$;[6] thus the external NO_3^- vibrations will be more highly hindered in the $LiNO_3$ lattice, and would be expected to exhibit higher frequencies.

SUMMARY

The polarized Raman spectrum of an anhydrous single crystal of $LiNO_3$ has been obtained under optimum experimental conditions. The Raman-active fundamental vibrations of the nitrate ion in the lattice have been established as follows: $\nu_4(E_g) = 735._4$, $\nu_1(A_{1g}) = 1071._0$ and $\nu_3(E_g) = 1384._6$ cm^{-1}. Several bands due to isotopic molecules and combinations of fundamentals were observed. The frequencies of the nitrate ion internal vibrations are essentially independent of the cation in the host lattice; thus there is no evidence to support the "free volume" theory for the frequency shifts advanced by Bues.[2] For some of the bands minor depolarization anomalies occur in the form of residual intensity in polarization orientations where Raman scattering is not expected according to symmetry. Although much of this intensity can be accounted for by the highly birefringent nature of the $LiNO$ crystal, it is clear that crystalline imperfections may also contribute.

This is demonstrated by the fact that $NaNO_3$, which has about the same birefringence, exhibited stronger anomalous depolarization[8] than $LiNO_3$. The predicted[9] sensitivity of the interference effects due to birefringence to the orientation of the crystalline sample is quite striking in the present example.

The Raman-active lattice modes of $LiNO_3$ have been obtained, and assigned to primarily translational ($124._4$ cm^{-1}) and librational ($237._2$ cm^{-1}) vibrations, respectively. No indication of coupling between these E_2 vibrations is observed. There is no evidence of an additional low-frequency torsional lattice mode. The frequencies of the external vibrations of the nitrate ion do depend strongly on the host lattices. Although the ratio of the libration/translation frequency is about the same in $LiNO_3$ as in $NaNO_3$, the values of the frequencies themselves are about 30% higher. A shift in this direction is quite reasonable in light of the significantly smaller unit cell volume of $LiNO_3$.

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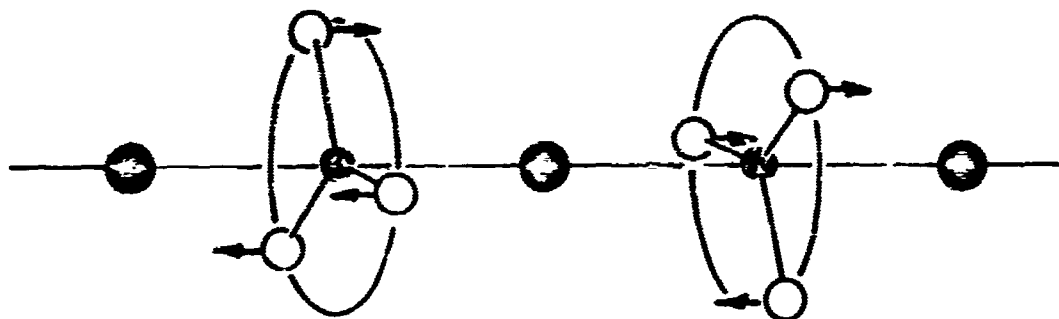TABLE I. Raman frequency shifts and relative magnitudes of polarizability derivatives for crystalline LiIO$_3$.

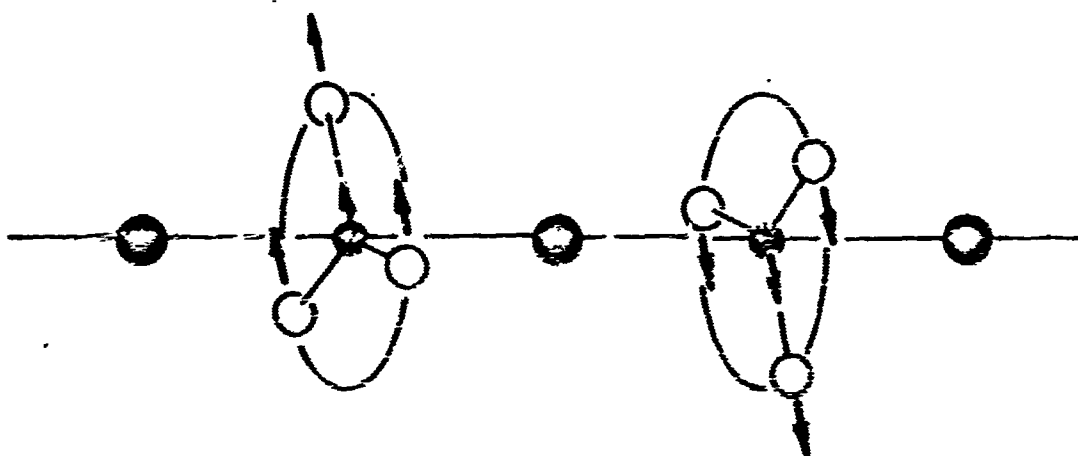| Symmetry Character	Frequency Shift (cm^{-1})	Allowed Polar- izability Changes	Expected Relative Magnitude	Observations
A$_{1g}$(ν_1)	1071.0	$\alpha_{xx} = \alpha_{yy}, \alpha_{zz}$	$\alpha_{xy}^2 > \alpha_{zz}^2$	$\alpha_{xx}^2 = 10\alpha_{zz}^2$
E$_g$(ν_3)	1384.6	$\alpha_{xx} = -\alpha_{yy} = \alpha_{xy}$	$\alpha_{xx}^2 >> \alpha_{xz}^2$	$\alpha_{xz}^2 = 0$
E$_g$(ν_4)	735.4	$\alpha_{xz} = \alpha_{yz}$	$\alpha_{xx}^2 >> \alpha_{xz}^2$	$\alpha_{xx}^2 >> \alpha_{xz}^2$
E$_g$(Lib)	237.2	$\alpha_{yx} = -\alpha_{yy} = \alpha_{xy}$; $\alpha_{xy} = \alpha_{yz}$	$\alpha_{xz}^2 >> \alpha_{xx}^2$; $\alpha_{xx}^2 = \alpha_{yy}^2 = \alpha_{xy}^2 = 0$	$\alpha_{xz}^2 = 400\alpha_{xx}^2$; $\alpha_{xz}^2 = 400\alpha_{zz}^2$
E$_g$(Trans)	124.4	$\alpha_{xx} = -\alpha_{yy} = \alpha_{xy}$; $\alpha_{xz} = \alpha_{yz}$	$\alpha_{xx}^2 >> \alpha_{xz}^2$; $\alpha_{xz}^2 = \alpha_{xy}^2 = 0$	$\alpha_{xz}^2 = 0$; $\alpha_{xx}^2 >> \alpha_{xz}^2$ $\alpha_{xx}^2 = \alpha_{xz}^2$ α_{xy}^2

Figure Captions

Fig. 1. The Raman-active lattice modes of crystalline $LiNO_3$. a. Libration. b. Translation.

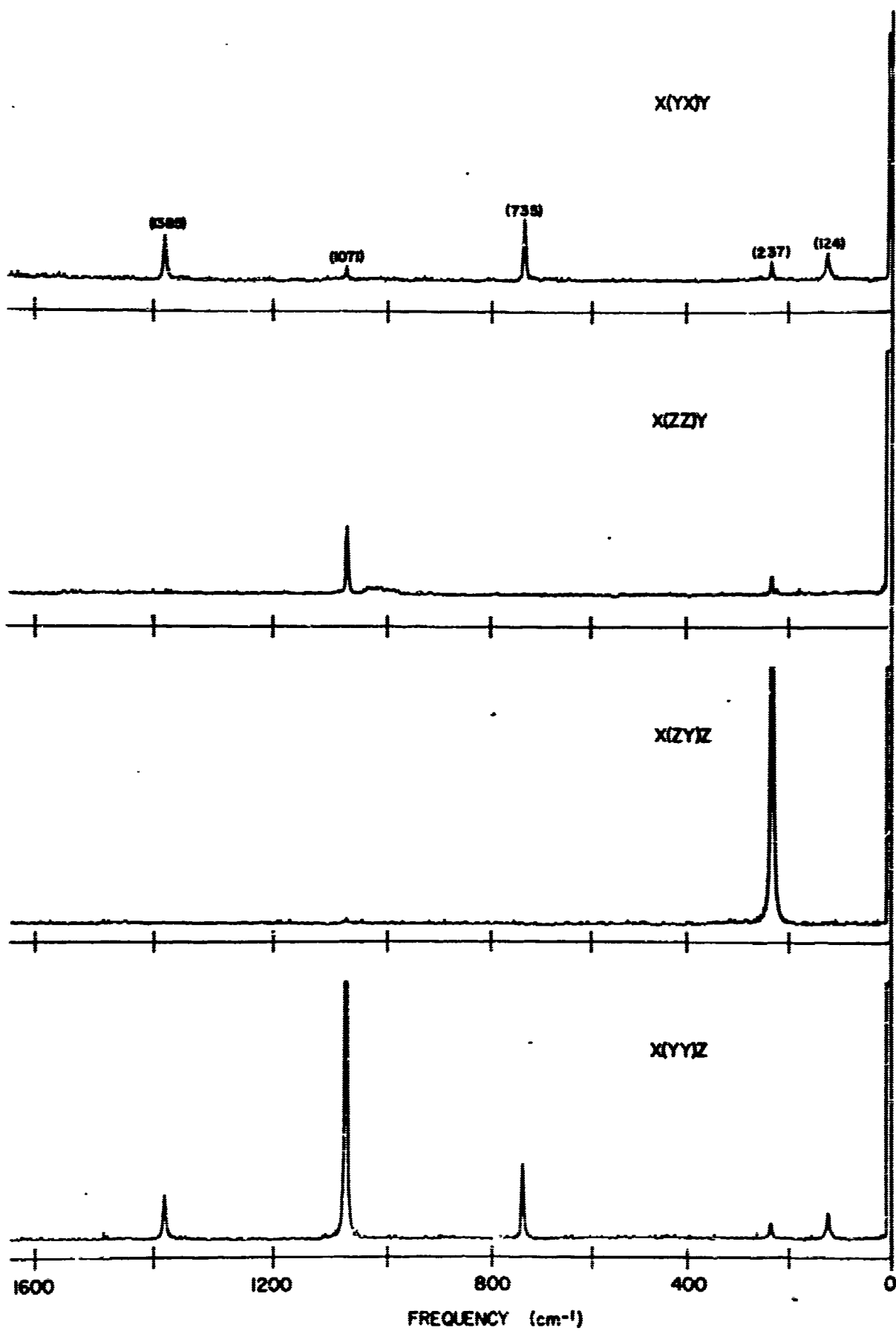Fig. 2. Raman Spectra of $LiNO_3$ in the four unique polarization orientations.

Fig. 3. The Raman spectrum of $LiNO_3$ in the xy-polarization as a function of crystal orientation.

(a)   (b)

X(YX)Y

(1580)   (1071)   (733)   (237)   (124)

X(ZZ)Y

X(ZY)Z

X(YY)Z

1600   1200   800   400   0

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13. ABSTRACT

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